

CLAIMS

1. Use of cobalt as a catalyst for heterocoupling between an aryl (pseudo)halide and a derivative that carries a double bond and a leaving group in vinyl-position, allyl-position and even homoallyl-position of said double bond by being brought into contact in a solvent with a metal or an alloy that is at least as reducing as zinc.
2. Use according to claim 1, characterized by the fact that the cobalt is present in oxidation state 2.
3. Use according to claims 1 and 2, wherein the cobalt is present in a coordinated form.
4. Use according to claim 3, wherein the coordination of the cobalt is carried out by a solvent compound or solvating compound that has a high donor index.
5. Use according to claim 4, wherein the atom that is responsible for a good donor index is selected from among the atoms of the nitrogen column.
6. Use according to claims 3 to 5, wherein the coordination of the cobalt is carried out by a specific coordinating agent.
7. Use according to claim 6, wherein said coordinating agent has functions that

are selected from among the pyridine, nitrile, phosphine, stibine and imine functions.

8. Use according to claims 1 to 7, wherein the metal is selected from among zinc and metals and alloys that are more electro-reducing than zinc.
9. Use according to claim 8, wherein the metal is selected from among manganese and metals that are at least as reducing as manganese, provided that when the metal is more electro-reducing than the manganese, the medium contains manganous ions.
10. Use according to claims 8 and 9, wherein said metal is selected from among the metals that are more electro-reducing than the manganese and wherein the medium contains manganous ions, advantageously at a concentration of between 2×10^{-3} and 10^{-1} M.
11. Use according to claims 1 to 10, wherein said derivative that carries a double bond and a leaving group is a vinyl ester.
12. Use according to claim 11, wherein the ratio of (coordinating agent(s)/cobalt) between coordinating agent(s), expressed in mol for the monodentates and in equivalent terms for the polydentates and the cobalt ions (expressed in mol) is at least equal to 0.5; advantageously 1, preferably 2 and more preferably 4.

13. Use according to claims 1 to 12, wherein said derivative that carries a double bond and a leaving group is an allyl ester or an allyl ether.
14. Use according to claim 13, wherein the ratio of [cobalt]/[coordinating agent that is at least bidentate and of which at least one tooth is pyridine expressed in pyridine equivalent] is greater than $\frac{1}{2}$, advantageously 1.
15. Use according to claim 14, wherein when the complexing agents are strong complexing agents, the cobalt/pyridine equivalent ratio is greater than $\frac{1}{2}$, advantageously 1.
16. Composition that comprises at least one cobalt salt, a solvent that is optionally conductive or made conductive, a cobalt coordinating agent and a derivative that carries a double bond and a leaving group.
17. Composition according to claim 16, wherein it also comprises a ferrous salt, advantageously in dissolved form.
18. Composition according to claims 16 and 17, wherein it comprises a ferrous salt, the Co/Fe ratio from 1/10 to 10/1, advantageously from 1/5 to 5/1.
19. Composition according to claims 16 to 18, wherein the cobalt content is between 2×10^{-3} et 10^{-1} M.

20. Composition according to claims 16 to 19, wherein it comprises a solvent that is selected from among the components below, alone or in a mixture:

- Purely oxidized solvents, in particular the ethers, preferably polyethers such as dimethoxy-1,2-ethane or cyclic ethers such as THF or dioxane;
- Amides, including ureas;
- Sulfones or sulfoxides;
- Nitrogen-containing derivatives, in particular nitrogen-containing heterocyclic compounds, in particular pyridine and compounds with nitrile functions;
- Complexing agents.

21. Composition according to claims 16 to 20, wherein the molar ratio of dissolved radical between the cobalt and a derivative that carries a double bond and a leaving group goes from 10^{-2} to 0.5.

22. Process of coupling an aryl (pseudo)halide with a derivative that carries a double bond and a leaving group, wherein it consists in subjecting a composition according to one of claims 16 to 19, also comprising an aryl (pseudo)halide to a reaction with a metal that is at least as electro-reducing as zinc.

23. Process according to claim 22, wherein the aryl (pseudo)halide is a compound of formula (I):



where X represents a halogen atom that is heavier than the fluorine, and

where Ar represents a homocyclic or heterocyclic aromatic radical.

24. Process according to claims 22 and 23, wherein the aryl (pseudo)halide is a compound of formula (I):



where X represents a bromine or chlorine atom, and

where Ar represents an aromatic radical whose core that carries X is stripped of electrons.

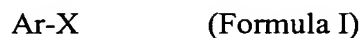
25. Process according to claims 22 to 24, wherein the aryl (pseudo)halide is a compound of formula (I):



where X represents a bromine or chlorine atom, and

where Ar represents an aromatic radical whose core that carries X is stripped of electrons and is selected from among the aromatic compounds of which said core carries electroattractor function(s) and/or group(s) and whose substituents are such that the sum of their Hammett constants σ_p (sigma p) is greater than zero.

26. Process according to claims 22 to 25, wherein the aryl (pseudo)halide is a compound of formula (I):



where X represents a chlorine atom, and

where Ar represents an aromatic radical whose core that carries X is stripped of electrons and is selected from among the aromatic compounds of which said core carries (an) electroattractor function(s) and/or group(s) and whose substituents are such that the sum of their Hammett constants σ_p (sigma p) is at least equal to 0.4, preferably 0.5 or of which said core is a heterocyclic compound with 6 chain links that advantageously have an atom from the nitrogen column, and especially nitrogen and phosphorus.

27. Process according to claim 23, wherein the aryl (pseudo)halide is a compound of formula (I):



where X represents a bromine or iodine atom, and

where Ar represents an aromatic radical whose core that carries X is not stripped of electrons.

28. Process according to claims 22 to 27, wherein said derivative that carries a double bond is a vinyl ester of formula (II)



[Formula II]

where R_1 , R_2 et R_3 , which may or may not be different, are selected from

among hydrogen, the functions that are more difficult to reduce than the function Y and from among the hydrocarbon radicals, in particular alkyls and aryls;

where Y corresponds to a leaving group that can exist in the form Y⁻,

5 advantageously selected from among the halogens and the carboxylates and wherein said metal or alloy is more electro-reducing than the zinc.

29. Process according to claim 28, wherein the cobalt is complexed by a bidentate coordinating agent, advantageously of which one of the teeth is a pyridine,
10 preferably of which the two teeth are pyridines, more preferably bipyridine.

30. Process according to claims 28 and 29, wherein said radical Ar is an acyloxyphenyl.

15 31. Process according to claims 28 and 30, wherein said vinyl acetate is selected from among the vinyl alcanoates per se (where R₁, R₂, and R₃ are H) and the isopropenyl alcanoates (one of R₁, R₂, and R₃ is methyl and the others are hydrogens).